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Highly selective halogenation of unactivated C(sp^3)-H with NaX under co-catalysis of visible light and Ag@AgX

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Abstract The direct selective halogenation of unactivated C(sp^3)–H bonds into C-halogen bonds was achieved using a nano Ag/AgCl catalyst at RT under visible light or LED irradiation in the presence of an aqueous solution of NaX/HX as halide source, in air. The halogenation of hydrocarbons provided mono-halide substituted products with 95% selectivity and yields higher than 90%, with the chlorination of toluene being 81%, far higher than the 40% conversion using dichlorine. Mechanism studies demonstrated that the reaction is a free radical process using blue light (450~500 nm), with visible light being the most effective light source. Irradiation is proposed to cause AgCl bonding electrons to become excited, electron transfer from chloride ion induces chlorine radical formation which drives the substitution reaction. The reaction provides a potentially valuable method for the direct chlorination of saturated hydrocarbons.

Introduction

The halogenation of C-Hs is an important industrial reaction used in the synthesis of bulk and fine chemicals.[1] Most current processes are performed by making use of either dihalogen or expensive *N*-halogensuccinimide (NXS) as halogenating agents for the halogenation of aromatic C-Hs, alkylarene α-Hs and alkylene α-Hs, or through classic functional group transformation from the corresponding alcohols, alkenes and carboxylic acids precursors.[2] In contrast, direct halogenation of C–H bonds with inorganic halide such as NaCl is an economically attractive and sustainable strategy, however, there are three unsolved problems with the reaction. Firstly, there is little difference between the various C-H bonds in alkanes in terms of relative reactivity, hence, few reagents can activate specific C-H bonds selectively in alkanes under mild reaction conditions to yield products with predictable and controllable results.[3] Secondly, the maximum yield of the alkylchloride based upon chlorine is only 50% with an equivalent of HCl formed as by-product. Thirdly, X_2 as the halogen source is a toxic gas or liquid, which is inconvenient and creates safety issues in operation. Most recently, it has been reported that palladium-catalyzed halogenation of unactivated C(sp^3)–H bonds (**Figure 1**) occurs at room temperature. This method can only be used to achieve the β-halogenation of carbonyl compounds and mono-chlorination of cyclohexane with NaClO (3:1) was also reported by the catalysis of base-resistant porphyrin metal–organic framework PCN-602m,[4] however, the reuse of the catalyst is a problem. Therefore, inventing a new halogenation reaction of unactivated C(sp^3)–H is an ideal target for synthetic chemical research aiming at both solving the above issues and finding a cheaper, secure, nontoxic halogenating agent.

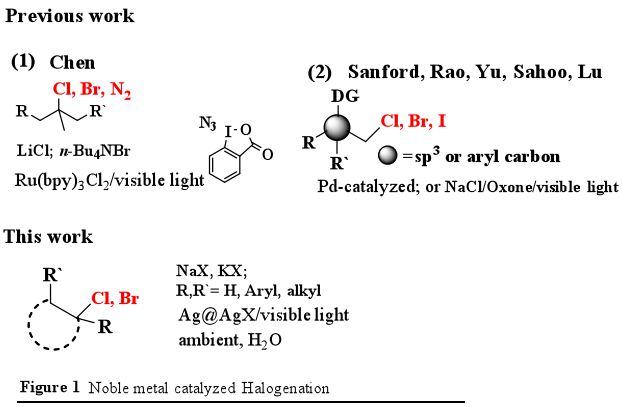

Figure 1 Noble metal catalyzed Halogenation

Sodium halide, such as NaCl, is the original and most common and non-toxic chlorine source, which is also a major feedstock for producing Cl_2, and chlorine compounds in general, in industry. However, when NaCl is employed directly as a chlorination agent for the chlorination of C-H bonds, the reaction was carried out by the transformation of the NaCl to Cl2 with an external and stronger oxidant, for example, oxone,. However, the selectivity is not good, especially for the chlorination of alkylbenzenes and a mixture of products

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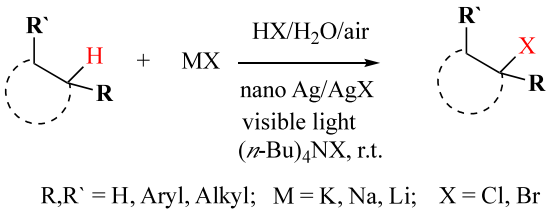
derived from both C(sp^3)–H and C(sp^2)–H chlorination were obtained.[5] At the same time, the waste resulting from the oxidation agents creates environmental, disposal and potentially, pollution issues. An ideal and sustainable strategy for halogenation of unactivated C-Hs with NaCl needs to be realized that uses air or O_2 as oxidant at room temperature and in H_2O, if at all possible.

In the past seven decades, an important goal for the future of the chemical industry is to develop sustainable, environmentally benign processes, which is a still emerging, attractive, challenging and current theme for sustainable chemistry.[6] Although the selective direct conversion of C-Hs into C-X functions (X = Cl, Br, C, O, N) under thermal conditions is generally not good, heterogeneous photocatalysis shows considerable promise to become the technology of choice, with transition-metal-catalyzed transformations arguably constituting the most valuable tool.[7] Recently, nano-hybrid visible light photoredox catalysis has become a promising strategy for the development of novel and sustainable C(sp^3)–H activation reactions.[8] Selective photocatalytic oxidation of various substrates has been achieved *via* photo-induced electron-transfer reactions of photocatalysts with substrates and dioxygen under visible light irradiation.[9] The insertion of hydroxyl function into aromatic C-Hs, alkene α-C-Hs, alkylarene α-Hs and α-C–H functionalization of amines, (het)aryl diazonium salts has been developed using air as a sustainable oxidant.[10],[11] A visible-light-promoted, radical halogenation of tertiary aliphatic C–Hs with halide using the Zhdankin reagent and $Ru(bpy)_3Cl_2$ as co-catalyst was also recently reported.[12] Nano-silver is an important component of composited photocatalysts and utilised in many organic reactions,[13] including for the degradation of organic waste.[14] For example, Ag@AgCl was employed as photocatalyst to catalyse chlorination of α-Hs in alkylarenes with a NaCl/HCl solution under sunlight or visible light induced conditions. [15]

As part of our ongoing interest in C(sp^3)–H reactions, we now report a highly selective halogenation of saturated C-Hs which is normally difficult to achieve using traditional halogenation dihalide reagents, which represents a novel, direct and selective halogenation of unactivated C(sp^3)–H bonds (**Scheme 1**). This report is especially applicable to different alkylarene and cyclic hydrocarbons, for example, the chlorination of toluene was achieved in 81% yield and that of cyclohexane in 78%, both reactions using Ag@AgCl as an efficient photocatalyst in the presence of an aqueous solution of NaX/HX as halogenating reagent source, in air and under visible light irradiation.



R,R` = H, Aryl, Alkyl; M = K, Na, Li; X = Cl, Br

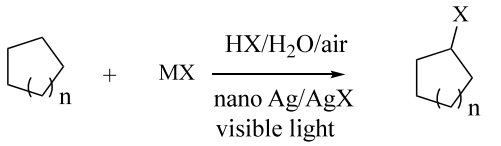
Scheme 1 The halogenation of C(sp^3)–H bonds

Results and discussion

Nanohybrid Ag@AgX (X = Cl or Br) is not only one of the most well known photocatalysts based on nano-Ag but is also a photocatalyst for the chlorination of alkylarene α-H.[13d] In order to achieve transformation of an unactivated C(sp^3)–H bond into C-halogen bonds, the preparation of the photocatalyst was improved using the glucose replacement, sodium formate. The loading level of nano-Ag@AgCl was 5.2-8.4 mol% and the nanohybrid Ag@AgBr level used was 4.5-5.6%, with both these nano-Ag catalysts being prepared using a similar methods.

Among alicyclic hydrocarbons, saturated 5-8 cyclic hydrocarbons are important fine chemicals, and hence, mono-halogenated analogues are especially useful. The direct halogenation of such compounds with X_2 usually results in mixtures of products. In contrast though, when cyclohexane was treated with a MCl/HCl (M = Li, Na, K) solution for 5 h under the photocatalytic nanohybrid Ag@AgCl and visible light (provided by a 300 W Xe arc lamp equipped with an ultraviolet cut-off filter) conditions, the corresponding chlorinated products were obtained with 38% conversion and pleasingly, the mono-chlorination product was obtained with 98% selectivity and 95% yield. This result shows that this approach has higher selectivity for the twelve Hs of the cyclohexane compared to the classical reaction. In addition, to improve the conversion and optimise the reaction, the method of use of the photocatalyst Ag@AgCl and how it was added was changed. Hence, when the photocatalyst was added in 3 - 5 batches, *i.e.* as the reaction proceeded, with the time between each addition being 2 h, the conversion of cyclohexane was considerably increased up to 78% with the loading level reaching 6.5 mol% of the nano Ag@AgCl catalyst in total. Under similar conditions, the chlorination of cyclopentane, cycloheptane and cyclooctane also all yielded mono-substituted products with exceptional selectivity, *i.e.* with conversions of 71%, 58% and 44%, respectively. The same substrates were also selected to examine the corresponding bromination reaction using MBr/HBr solution as bromide source under the photocatalytic nanohybridAg@AgBr and visible light conditions; the results are exhibited in the Table 1.

Table 1 Halogenation of saturated 5~8 alicyclic hydrocarbons



M = K, Na, Li n = 1,2,3,4

	X = Cl			X = Br		
Entry	Conv. (%)*	Select. (%)*	Yield (%)	Conv. (%)*	Select. (%)*	Yield (%)
1	71	96	94	62	95	92
2	78	98	95	72	97	93
3	58	96	90	55	94	83
4	44	75	72	50	95	86

*The conversions are based on GC-MS; the selectivities are based on ^{1}H NMR

This data in Table 1 shows that the conversion to chlorination products was higher than for bromination products, for the same substrates. The conversion and selectivity of the halogenated products was variable, depending on the ring size. Also, the conversion of cyclohexane was highest out of all of the saturated alicyclic hydrocarbons (5 - 8 membered-ring sizes) with the conversion of cyclooctane being the lowest. However, the selectivity of the halogenations for the substrates shown in Table 1 was high, with mono-halogenated products being obtained with greater than 95% selectivity, except for the chlorination of cyclooctane. According to the ^{1}H NMR of the cyclooctane chlorination reaction mixture, multiple peaks were observed between 5.60-5.58 ppm showing that many by-products related to cyclooctenes were being produced.

In the halogenation of cyclohexane, the stability of the catalyst was investigated. With a loading level of 5.6 mol% of nano Ag@AgCl, *i.e.* in a catalytic amount of the catalyst, the halogenation of cyclohexane was carried out six times. The results are shown in the Table 2 and show that the catalyst was highly stable and that the catalytic activities remained essentially constant after each of the reactions on all six occasions. Indeed, the conversion, selectivity and yield for all six chlorinations and brominations were almost unchanged, and importantly, the weight of the recovered catalyst only decreased by 0.12% after all six cycles.

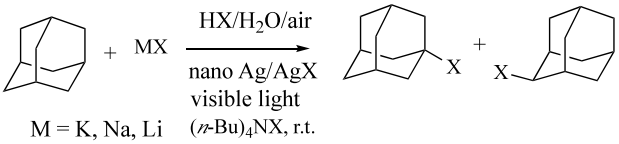
Table 2 The result of cyclohexane halogenation with the loading level 5.6 mol% of nano-Ag at AgCl as catalyst

	X = Cl			**X = Br**		
Entry	Conv. (%)*	Select. (%)*	Yield (%)	Conv. (%)*	Select. (%)*	Yield (%)
1	76	96	95	70	92	91
2	76	96	94	72	95	93
3	75	98	95	72	97	92
4	77	95	95	71	95	92
5	75	96	96	69	94	90
6	75	96	93	71	93	91

*The conversions are based on GC-MS; the selections are based on ^{1}H NMR

Adamantane, an aliphatic bridged-ring compound containing four tertiary-Hs and twelve secondary-Hs, was also exposed to the MX/HX solution conditions, under the nanohybrid Ag@AgX photocatalytic conditions at room temperature. Halogenation occurred readily in 78% conversion for chlorination and 62% conversion for bromination, respectively, as shown in **Table 3.** For the chlorination, the result was a mixture containing two monohalides. GC-MS showed that the proportion of two products was about 3:2, and NMR and MS of the products showed that one product had a tertiary-hydrogen replaced and another was secondary substituted product.[16] There were notably no dihalide products, and again, good chemoselectivity for the monohalogenation was exhibited, with the bromination of adamantane giving 62% conversion, however, ^{1}H NMR and GC-MS of the reaction mixture showed that the selectivity was so high that the product was almost entirely the tertiary-H substituted product. These results demonstrate that the halogenation system selects the C(sp^3)-H in substantial preference to other Hs.

Table 3 Halogenations of adamantine

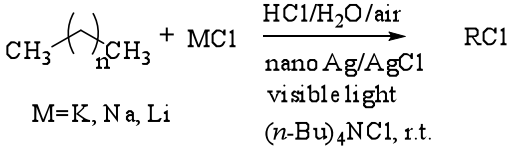


X	Conversion (%)*	Selection (%)*		Yield
Cl	76	58	42	92%
Br	62	95	5	88%

* The conversions are based on GC-MS

Taking these results further, the halogenations of unactivated C(sp^3)-Hs in open-chain alkanes using the inorganic halide as halogenating reagent under nanohybrid Ag@AgX and visible light co-catalysis was also examined. The results of these experiments are shown in **Table 4**. When *n*-pentane was treated with a MCl/HCl solution using the nanohybrid Ag@AgCl as photocatalyst under λ≥ 400 nm visible light irradiation at room temperature, chlorination of the *n*-pentane took place readily and three mono-chlorination products were observed according to GC-MS and ^{1}H NMR, in a 3:4:2 ratio of 1-Cl-pentane, 2-Cl-pentane and 3-Cl-pentane, respectively. Most importantly, no dichloride substituted products were detected. The chlorination products of *n*-hexane were similar to the results for *n*-pentane, however, the ratio of the three mono-chlorides was 1:1:1, with a total conversion of 47%.

Table 4 Halogenation of chain alkane



n	R	Conversion (%)*	Selection (%)*
3	*n*-pentyl	33	34
	s-pentyl		42
	3-pentyl		24
4	*n*-hexyl	47	33
	s-hexyl		34
	3-hexyl		33

* The conversions are based on GC-MS; the selections are based on ^{1}H NMR.

Mechanism and further examples

The halogenative functionalization of saturated C-Hs with the KX/HX solution under nanohybrid Ag@AgX photocatalytic conditions at room temperature is a multi-phase reaction system. The mechanism is likely complex, although chloride radical is considered to be formed during the decomposition of organic contaminants of photocatalysis over Ag@AgCl under visible light. A possible mechanism for toluene chlorination has already been

proposed by us,[15] however, there was no experimental evidence to back up these claims. Herein, we report a series of experiments designed to demonstrate a likely involvement of the key halide radicals and halide molecules in the different reactions, caused by light under the halogenation conditions.

According to the likely free radical mechanism, halide radical is essential in order to carry out the halogenation. When visible light activates the nano Ag catalyst, a photon is absorbed, producing an excited state, and a valence electron from an Ag atom on the Ag@AgCl catalyst forms an empty orbital (hole) on the catalyst surface making it able to accept an electron from Cl^- ion on the AgCl. The result is the formation of a Cl^0 atom. The photogenerated electron is transferred to O_2 dissolved in the water. The loss of a chloride ion from the catalyst is compensated for immediately by chloride from the solution, resulting in the continual production of chlorine radicals under the reaction conditions. In order for this electron transfer method to trigger radical formation to take place at the interface between the solid and liquid phases, the formation of the halide radical has to be kinetically limited. Hence, the selectivity of the halogenations is higher than that for the traditional halogenation with X_2. The role of HX in the halogenation agents "MX/HX", are twofold: 1) providing the acidic conditions to inhibit the substitution of the C-X function in the halogenation products; and 2) to neutralize the base resulting from decreasing the concentration of X^- in the MX solution. The postulated mechanism is shown in **Figure 2.**

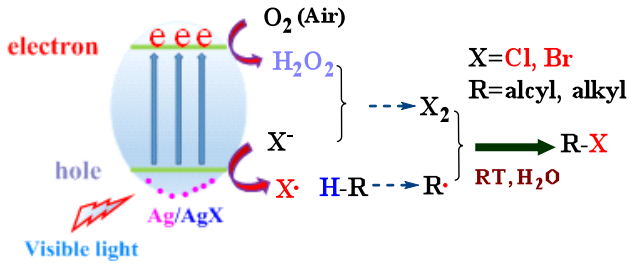
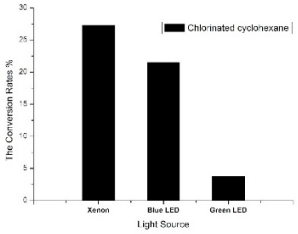


Figure 2 The possible mechanism

In order to determine the effect of the light source on the halogenations, three types of light were selected to execute the chlorination of cyclohexane. **Figure 3a** shows a comparison between using the different light sources for irradiating the reaction involving the Ag@AgCl catalysed reaction to initiate the chlorination process. The xenon light source was most effective (>400 nm), with the blue light LED-produced light (476 - 495 nm) being the next most effective light source, while the longer wavelength green light (495 - 570 nm) was least effective for catalysing the reaction. Interestingly, yellow light (570 - 590 nm) had almost no effect upon the reaction. In the absence of any heating effects from these light sources, it is clear that only the photons from the light initiate the halogenation reactions.

We previously reported the light induced selective chlorination of the α-Hs in toluene with a NaCl/HCl solution using Ag@AgCl. In fact, when Ag@AgBr was used as photocatalyst to catalyse the reaction of toluene or ethylbenzene with KBr/HBr solution, the corresponding mono-bromide was observed by GC after 5 h. Under the same conditions, when Ag@AgCl was used as photocatalyst for the bromination of toluene or ethylbenzene, the corresponding α-bromide compound was obtained, and the corresponding α-chloride product was also formed (see SI for NMR data). Table 5 summarises these results.



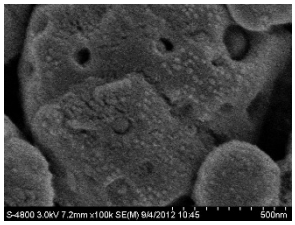
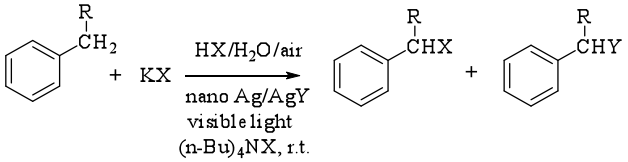


Figure 3a. Effect of light source on the chlorination of cyclohexane; b. SEM of Ag/AgCl after catalytic reaction

Table 5 The halogenation of alkylarenes

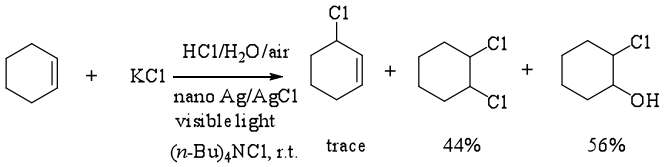


Reaction	X,Y	Cat.	R	Conv. (%)*	Yield (%)#
Chlorination	X=Y=Cl	Ag/AgCl	H	81	94
			CH_3	74	91
	X=Cl Y=Br	Ag/AgBr	H	trace	
			CH_3	trace	
Bromination	X=Br Y=Cl	Ag/AgCl	H	73	90
			CH_3	52	86
	X=Y=Cl	Ag/AgBr	H	69	88
			CH_3	—	—

In contrast, using the Ag@AgBr catalyst resulted in almost no formation of toluene chlorination products. Clearly, the two types of photocatalyst have quite different catalytic properties, presumably because the electronic potential of halogen radical produced by visible light irradiation is different in the two systems. The higher electronic potential chloride radical produced from Ag@AgCl can oxidize bromide ion to the lower electronic potential bromide radical to carry out the subsequent bromination of alkylbenzene α-H. However, the opposite process does not occur. Although XRD (see Supplementary Information) of the photocatalyst after the bromination with Ag@AgCl catalysis shows that Ag@AgBr was formed by the exchange of halide ion; the chlorine radical that results in the chlorination products formed is actually provided only from AgCl during the bromination. Additionally, **Figure 3b** shows that after the reaction was complete, different cavities were formed on the surface of the Ag@AgCl catalyst, revealing the loss of AgCl from the catalyst surface, presumably caused by chloride ion transferring an electron, and transforming onto chlorine radical, with the silver ion being reduced *in-situ* to silver metal. All these results confirm that halogen radical

formation is the most likely process occurring, resulting in the halogenated products observed.

Further reinforcement of the proposed mechanism was obtained when cyclohexene was reacted with the KCl/HCl solution under visible light using the nanoAg@AgCl photocatalyst at room temperature. In this case, a mixture of products resulted, as shown in **Scheme 2**. However, GC-MS showed that 1,2-dichlorocyclohexane and 2-chlorocyclohexanol were the main products, with the α-H substituted product present in only trace amounts. This result reveals that dichlorine is formed during the reaction, however, Cl_2 (gas) was not detected. Thus, at the lower concentrations under which the dichlorine is generated, the alkene addition reaction is favoured over the radical-based CH abstraction/halogenation. Also, the halogenation is strongly dependent upon the presence of air and does not take place in an inert, e.g. N_2, atmosphere. Dioxygen in air is the acceptor of the photogenerated electron and when O_2 is reduced (to H_2O_2 which oxidize Cl^- to Cl_2 to keep the chlorination), it can also act as an oxidizing agent to give the epoxide, which reacts further with hydrochloric acid to give the chlorohydrin product observed.



Scheme 2 The chlorination reaction of cyclohexene

Based on the proposed mechanism, the reaction has been expanded to the chlorination of many substituted alkylarene α-Hs. Figure 4 shows a further seven examples, demonstrating that the selectivity and yields of these substrates were excellent, with chlorination being higher than 80%, except for the *p*-t-Bu toluene chlorination. Even the selectivity for 4,4`-dimethylbiphenylmonochlorination also was higher than 92% and the conversions for these reactions were in the region of 66-83%. These results clearly reinforce major advantages of this halogenation approach over the traditional methods used such as with Cl_2 as chlorination agent.

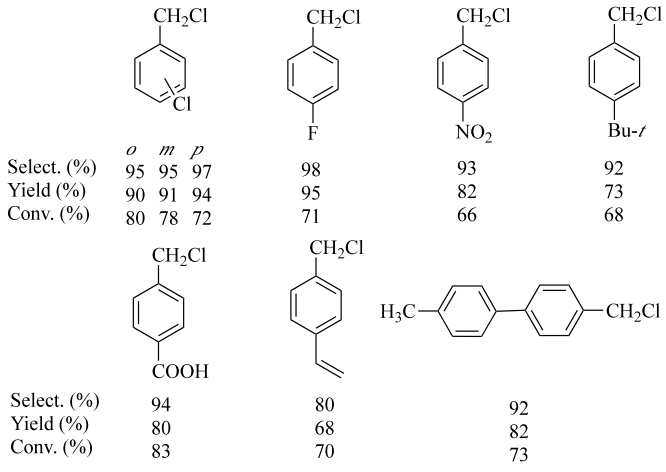


Figure 4 Yield, conversion and selectivity for the chlorination of substituted alkylarenes

Experimental

General procedure

The morphology of the Ag@AgX (X = Cl, Br) composite was characterized using a scanning electron microscope (SEM; Hitachi S4800 SEM) with an accelerating voltage of 30.0 kV. The crystallinity was determined by X-ray diffraction (XRD) using a diffractometer with Cu Kαradiation (Shimadzu Lab-X XRD-6000). The accelerating voltage and applied current were 40 kV and 30 mA. The composition was verified by energy dispersive X-ray analysis (EDX, equipped with SEM JSM-6360LV). The light absorption properties were measured using UV–vis diffuse reflectance spectrophotometer (DRS, JASCO, UV-550) with a wavelength range of 200–900 nm. The output power of xenon lamp (300 W Xe arc lamp**,** λ >290 nm, PLS-SXE300CUV, perfect light Instruments Co. Ltd., Beijing) used as light source is 50W, and the average light intensity was 78.5 mw/cm−2. The power of blue LED lamp is 15W. Quantitative and qualitative analysis of the chlorinated and brominated product with GC-MS (ISQ QD) and ^{1}HNMR and ^{13}CNMR. NMR were recorded on a BrukerAvance II 500 spectrometer in $CDCl_3$ unless stated otherwise, using tetramethylsilane as an internal reference, operated at 500 for ^{1}H, operated at 125 for ^{13}C, and J values are given in Hz. All chemicals used in this study were commercially available without further purification unless otherwise noted.

Preparation of catalysts

(1) The Ag@AgCl photocatalyst was prepared according to the references 13(d), the loading level of nano Ag at AgCl is 5.2-8.4mol%.

(2) Ag@AgBr photocatalyst

In a typical case, $AgNO_3$ (3.0 mmol) and 0.625 g polyvinyl pyrrolidone (PVP, K30) were dissolved in 50 mL of 1.0 M nitric acid solution under magnetic stirring at room temperature. Then 50 mL of 0.06 M KBr aqueous solution was added to it dropwise 45 min later. The mixture was stirred and heated at 65 °C for another 30 min. After completion of the reaction, the precipitated AgBr was collected by centrifugation and washed with distilled water, dispersed in a solution of distilled water (50 mL) and $AgNO_3$ (0.10 g) and irradiated with UV irradiation for 20 min in the presence of glucose (1 mL, 0.1 M) to reduce adsorbed Ag^+ to Ag^0 via $AgNO_3$ photolysis. The resulting product was collected and washed thoroughly with distilled water and absolute ethanol and then dried at 45 °C for 12 h. The loading level of nano-Ag in AgBr was 4.5-5.6 mol%.

The photocatalytic halogenation of alicyclic hydrocarbon

The phase transfer catalyst TBAC or TBAB (1.2 mmol) was dissolved in alicyclic hydrocarbon (0.5 mol) and the solution was transferred into a photocatalytic reaction vessel (PLS-SXE300CUV). Saturated potassium chloride or bromide solution (60 ml) containing hydrochloric acid (6 ml) or 48% hydrobromic acid (5 ml) was added to the above solution. Visible light produced by a 300 W xenon lamp equipped with an ultraviolet cut-off filter or LED lamp was used as the light source to irradiate the reaction mixture. The photocatalyst Ag@AgX (0.65 g - 1.02 g) was added in 3-5 batches to

the reaction vessel, with each addition being at 2 h intervals, as reaction proceeded. The reaction was monitored by GC. After the reaction was complete (about 6–9 h), the reaction solution was filtered to reclaim the photocatalyst and the residual solution was separated. The aqueous/inorganic phase was collected for future use in further reactions and the organic phase was dried ($MgSO_4$) and the halogenation product obtained by distillation.

Chlorination of cyclopentane

Product (CAS registry No: 930-28-9) was obtained according to the general procedure in 71% conversion and 94% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.32-4.39 (m, 1H), 1.92-2.01 (m, 2H), 1.82-1.89 (m, 4H), 1.67-1.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 62.1, 37.1 (2C), 23.0 (2C); GC-MS (m/z) 105.1 $[M+H]^+$ (cald for C_5H_9Cl , 104.04).

Bromination of cyclopentane

Product (CAS registry No: 137-43-9) was obtained according to the general procedure in 62% conversion and 92% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.35-4.38 (q, *J*= 4.5 Hz, 1H), 1.99-2.01 (m, 4H), 1.81-1.85 (m, 2H), 1.56-1.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 53.4, 37.9 (2C), 25.8 (2C); GC-MS (m/z) 148.1 $[M]^+$ (cald for C_5H_9Br, 148.0).

Chlorination of cyclohexane

Product (CAS registry No: 542-18-7) was obtained according to the general procedure in 78% conversion and 95% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.96-4.01 (m, 1H), 2.03-2.07 (m, 2H), 1.69-1.82 (m, 2H), 1.61-1.68 (m, 2H), 1.50-1.54 (m, 1H), 1.32-1.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 60.0, 36.7 (2C), 25.2 (2C), 24.8; GC-MS (m/z) 118.10 $[M]^+$ (cald for $C_6H_{11}Cl$, 118.05).

Bromination of cyclohexane

Product (CAS registry No: 108-85-0) was obtained according to the general procedure in 72% total conversion and 93% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.16-4.20 (m, 1H), 2.13-2.16 (m, 2H), 1.76-1.86 (m, 5H), 1.56-1.58 (m, 2H), 1.33-1.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 53.1, 37.6 (2C), 25.9, 25.2 (2C); GC-MS (m/z) 162.10 $[M]^+$ (cald for $C_6H_{11}Br$, 162.00).

Chlorination of cycloheptane

Product (CAS registry No: 2453-46-5) was obtained according to the general procedure in 58% conversion and 90% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.11-4.14 (m, 1H), 2.08-2.14 (m, 2H), 1.82-1.90 (m, 2H), 1.67-1.71 (m, 2H), 1.45-1.53 (m, 4H), 1.37-1.44 (m, 2H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 62.8, 31.0 (2C), 27.7 (2C), 24.8 (2C); GC-MS (m/z) 132.00 $[M]^+$ (cald for $C_7H_{13}Cl$, 132.07).

Chlorination of cyclooctane

Product (CAS registry No: 2453-46-5) was obtained according to the general procedures at 44% conversion and 72% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.10-4.16 (m, 1H), 1.99-1.93 (m, 2H), 1.77-1.72 (m, 2H), 1.63-1.58 (m, 4H), 1.48-1.51 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 63.3, 35.2 (2C), 27.5 (2C), 25.0, 23.6 (2C); GC-MS (m/z): 146.10 [M]+ (cald for C8H15Cl, 146.09), 82.1 ([M]+-C2H5Cl).

Bromination of cyclooctane

Product (CAS registry No: 1556-09-8) was obtained according to the general procedure in 50% conversion and 89% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.42-4.37 (m, 1H), 2.41-2.19 (m, 2H), 2.16-2.07 (m, 3H), 1.78-1.71 (m, 3H), 1.59-1.52 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 57.4, 36.0, 35.2, 27.5, 26.8, 25.1, 24.8, 23.7; GC-MS (m/z) 111.2 $([M+1]^+$-HBr) (cald for $C_8H_{15}Br$, 190.04).

The photocatalytic halogenation of adamantane

The phase transfer catalyst TBAC (1.5 mmol) and Ag@AgX photocatalyst (0.8 g) were suspended and dissolved in the solution of fluorobenzene and adamantane (0.3 mol), and the solution was transferred into a photocatalytic reaction vessel (PLS-SXE300CUV). Saturated potassium chloride or bromide solution (60 ml) containing hydrochloric acid (6 ml) or 48% hydrobromic acid (5 ml) was added. The visible light produced by a 300 W xenon lamp equipped with an ultraviolet cut-off filter or LED lamp was used as light source to irradiate the reaction mixture for 6-8 h and the reaction was monitored by GC. Upon completion, the reaction solution was filtered to reclaim the photocatalyst, and the solution separated. The inorganic/aqueous phase was collected for future use and the organic phase was dried ($MgSO_4$) and the solid product obtained by evaporation. GC-MS showed the conversion of adamantane was 76%, the ratio of 1-chloroadamantane and 2-chloroadamantane was approximately 4:3, and the yield of two chlorination products was 92%. The ratio of 1-bromoadamantane and 2-bromoadamantane was approximately 95:5, obtained in a yield of 88%.

Chlorination of adamantane

1-Cl-adamantane (CAS registry No: 935-56-8), 53%, mp. 164.5-166^{o}C.^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.14 (s, 9H), 1.68 (s, 6H); ^{13}CNMR ($CDCl_3$, 125 MHz) δ 69.1, 47.9 (3C), 35.7 (3C), 31.9 (3C); GC-MS (m/z) 170.10 $[M]^+$ (cald for $C_{10}H_{15}Cl$, 170.09), 135 (M^+ - Cl).

2-Cl-adamantane (CAS registry No: 7346-41-0), 39%, mp. 192~195 ^{o}C.^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.39 (s, 1H), 2.28~ 2.26 (d, J = 12.5Hz, 2H), 2.14 (s, 2H), 1.96~1.95 (d, *J* = 2.5Hz, 2H), 1.78~1.76 (d, *J* = 10.0 Hz, 4H), 1.58~1.56 (d, *J* = 10.0Hz, 4H); ^{13}CNMR ($CDCl_3$, 125 MHz) δ 68.4, 38.3 (2C), 37.8, 35.9 (2C), 31.1 (2C), 27.5, 27.0; GC-MS (m/z) 170.10 [M]+ (cald for C10H15Cl , 170.09), 134.1 (M + - Cl).

Bromination of adamantine

1-Br-adamantane (CAS registry No: 768-90-1), 84%, mp. 164.5-166 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35-2.34 (d, *J* = 3.0 Hz, 6H), 2.09 (s, 3H), 1.75-1.71 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 66.8, 49.4 (3C), 35.6 (3C), 32.7 (3C); GC-MS (m/z) 215.00 $[M+1]^+$ (cald for $C_{10}H_{15}Br$, 214.04), 135.2 ($[M+1]^+$ - HBr).

The photocatalytic chlorination of alkanes

TBAC (1.5 mmol) and Ag@AgCl photocatalyst (0.9 g) was suspended and dissolved in the hydrocarbon (0.5 mol) and the solution was transferred into a photocatalytic reaction vessel (PLS-SXE300CUV). The mixture solution (50 ml), containing saturated potassium chloride (45 ml) and hydrochloric acid (5 ml) was added to the above solution. Blue light produced by an LED lamp was used as light source to irradiate the reaction mixture for 5-8 h and the reaction was monitored by GC. The reaction solution was filtered to reclaim the photocatalyst and the remaining solution separated. The inorganic/aqueous phase was collected for future use and the organic phase was dried ($MgSO_4$) and the halogenation products obtained by distillation.

Chlorination of n-pentane

The chlorination products were mixture contained 1-Cl-pentane, 2-Cl-pentane, and 3-Cl-pentane. The yield was 86%, the ratio was approximately 3:4:2 successively.

1-Cl-pentane (CAS registry No: 543-59-9), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.49-3.54 (t, *J* = 7.0 Hz, 2H), 1.81-1.77 (m, 2H), 1.29-1.36 (m, 4H), 0.85-0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.5, 42.6, 25.4, 20.0, 13.6; GC-MS (m/z) 106.0 $[M]^+$ (cald for $C_5H_{11}Cl$, 106.05), 70.2 (M^+ - Cl).

2-Cl-pentane (CAS registry No: 625-29-6), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.04-3.97 (m, 1H), 1.51-1.50 (d, *J* = 2 Hz, 3H), 151-1.59 (m,

2H), 1.39-1.30 (m, 2H), 0.91-0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 45.1, 32.5, 29.2, 22.1, 14.0; GC-MS (m/z) 106.0 $[M]^+$ (cald for $C_5H_{11}Cl$, 106.05), 70.2 (M^+ - Cl).

3-Cl-pentane (CAS registry No: 616-20-6), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.78-3.73 (m, 1H), 1.74-1.59 (m, 4H), 1.07-1.03 (t, J = 3.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 67.4, 31.2(2C), 11.00 (2C); GC-MS (m/z) 106.0 $[M]^+$ (cald for $C_5H_{11}Cl$, 106.05), 70.2(M^+ - Cl).

Chlorination of n-hexane

The chlorination products were mixture contained 1-Cl-hexane, 2-Cl-hexane, and 3-Cl-hexane. The yield was 90%, the ratio was approximately 1:1:1 successively.

1-Cl-hexane (CAS registry No: 544-10-5), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.53-3.50 (t, J = 7Hz, 2H), 1.79-1.74 (m, 2H), 1.43-1.47(m, 2H), 1.35-1.32 (m, 2H), 1.02-1.05 (m, 2H), 0.93-0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 45.0, 32.7, 31.2, 26.7, 22.3, 13.6; GC-MS (m/z) 120.1 $[M]^+$ (cald for $C_6H_{13}Cl$, 120.07).

2-Cl-hexane (CAS registry No: 638-28-8), ^{1}H NMR ($CDCl_3$, 500 MHz): δ4.04-3.97 (m, 1H), 1.54-1.52 (m, 2H), 1.50-1.49 (d, *J* = 6.5Hz, 3H), 1.31-1.29 (m, 4H), 1.02-0.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.7, 40.3, 28.9, 25.4, 22.6, 14.0; GC-MS (m/z) 120.1$[M]^+$ (cald for $C_6H_{13}Cl$, 120.07), 85(M^+-Cl).

3-Cl-hexane (CAS registry No: 2346-81-8), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.86-3.81 (m, 1H), 1.72-1.67 (m, 4H), 1.45-1.42 (m, 2H), 1.06-1.02 (m, 3H), 0.94-0.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 65.4, 40.2, 31.6, 19.8, 14.0, 10.9; GC-MS (m/z) 120.1 $[M]^+$ (cald for $C_6H_{13}Cl$, 120.07), 85 (M^+-Cl).

The photocatalytic halogenation of (substituted) alkylbenzene

The phase transfer catalyst TBAC or TBAB (1.2 mmol) was added to the photocatalytic reraction vessel (PLS-SXE300CUV) and charged with the alkylarene (0.5 mol). Saturated sodium chloride or potassium bromide solution (60 ml) containing concentrated hydrochloric acid or hydrobromic acid (6 ml) was added with vigorous stirring to the above solution. A 300 W xenon lamp was used as light source to irradiate the reaction mixture. The photocatalyst Ag@AgCl (0.90 g) or Ag@AgBr (1.3 g)was added in 3 batches to the reaction vesselat intervals of 1-2 h, as reaction proceeded. The reaction was monitored by GC and after the reaction completed (about 5–8 h), the reaction solution was filtered to reclaim the photocatalyst, and the solution separated. The inorganic/aqueous phase was collected for future use and the organic phase was dried ($MgSO_4$), filtered and evaporated to provide the chlorinated product.

(1) Chlorination of toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give $PhCH_2Cl$ (CAS registry No: 100-44-7) at 81% conversion and 94% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.38-7.30 (m, 5H), 4.56 (s, 2H); GC-MS (m/z) 126.1 $[M]^+$ (cald for C_7H_7Cl , 126.02).

(2) Chlorination of ethylbenzene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give $PhCHClCH_3$ (CAS registry No: 672-65-1) at 74%conversion and 91% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41-7.32 (m, 5H), 5.10-5.05 (q, *J* = 6.5 Hz, 1H), 1.84-1.83 (d, *J* = 6.5 Hz, 3H); GC-MS (m/z) 140.1 $[M]^+$ (cald for C_8H_9Cl, 140.04).

(3) Bromination of toluene

a) The reaction was carried out according to the general procedure using Ag@AgBr as catalyst to $PhCH_2Br$ (CAS registry No: 100-39-0) at 69% conversion and 92% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.28 (m, 5H), 4.42 (s, 2H); GC-MS (m/z) 172.0 $[M+H]^+$(cald for C_7H_7Br, 171.03).

b) The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give $PhCH_2Br$ and $PhCH_2Cl$ at 73% conversion and the yield of $PhCH_2Br$ was 90%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.28 (m, 5H), 4.74 (s, 2H), 4.64 (s, 2H). GC-MS (m/z) 172.0 $[M+H]^+$ (cald for C_7H_7Br , 171.03), 126.1$[M]^+$ (cald for C_7H_7Cl, 126.02).

(4) Bromination of ethylbenzene

The reaction was carried out according to the general procedure using Ag@AgBr as catalyst to give $PhCHBrCH_3$ (CAS registry No: 585-71-7) at 52% conversion and 86% yield. ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.61-7.42 (m, 5H), 5.37-5.33 (q, *J* = 7.0 Hz, 1H), 2.21-2.19 (d, *J* = 7.0 Hz, 3H); GC-MS (m/z) 186.0 $[M+H]^+$ (cald for C_8H_9Br , 183.99).

(5) Chlorination of 2-Cl-toluene

The reaction was carried out according to the general procedures using Ag@AgCl as catalyst to give 2-Cl-$PhCH_2Cl$ (CAS registry No: 611-19-8) at 80%conversion and 90% yield. ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.43-7.41 (q, *J* = 3.5Hz, 1H), 7.36-7.34 (q, J= 3.5Hz, 1H), 7.23-7.19 (m, 2H), 4.65 (s, 2H). GC-MS (*m/z*) 160.0 $[M]^+$ (cald for $C_7H_6Cl_2$, 159.98).

(6) Chlorination of 3-Cl-toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 3-Cl-$PhCH_2Cl$ (CAS registry No: 620-20-2) at 78%conversion and 91% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (s, 1H), 7.30-7.28 (m, 3H), 4.54 (s, 2H); GC-MS (*m/z*) 160.0 $[M]^+$ (cald for $C_7H_6Cl_2$, 159.98).

(7) Chlorination of 4-Cl-toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 4-Cl-$PhCH_2Cl$ (CAS registry No: 104-83-6) at 72%conversion and 94% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.31-7.29 (d, *J* = 2.0 Hz, 2H), 7.24-7.21 (m, 2H), 4.53 (s, 2H); GC-MS (*m/z*) 160.1 $[M]^+$ (cald for $C_7H_6Cl_2$, 159.98).

(8) Chlorination of 4-F-toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 4-F-$PhCH_2Cl$ (CAS registry No: 352-11-4) at 71% conversion and 95% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ7.39-7.36 (q, J = 5.5 Hz, 3Hz, 2H), 7.07-7.04(t, J = 8.5 Hz, 2H), 4.58 (s, 2H); GC-MS (m/z) 144.00 $[M]^+$ (cald for C_7H_6F, 144.01).

(9) Chlorination of 4-NO_2-toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 4-NO_2-$PhCH_2Cl$ (CAS registry No: 100-14-1) at 66% conversion and 82% yield. GC-MS (m/z) 171.0 $[M]^+$ (cald for $C_7H_6ClNO_2$, 171.01).

(10) Chlorination of 4-t-Bu-toluene

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 4-*t*-Bu-$PhCH_2Cl$ (CAS registry No: 19692-45-6) at 68%conversion and 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.37 (d, *J* = 8.5 Hz, 2H), 7.20 (s, 2H), 4.54(s, 2H), 1.41 (s, 9H); GC-MS (*m/z*) 182.1 $[M]^+$ (cald. for $C_{11}H_{15}Cl$, 182.09).

(11) Chlorination of p-methylbenzoic acid

The reaction was carried out in fluorobenzene according to the general procedure using Ag@AgCl as catalyst to give 4-$ClCH_2$-PhCOOH (CAS registry No: 1642-81-5) at 83% conversion and 80% yield. ^{1}H NMR (CD_3OD, 500 MHz): δ 8.02-8.00 (d, J=10.0 Hz, 2H), 7.52-7.50 (d, J=10.0 Hz, 2H), 4.69 (s, 2H); GC-MS (*m/z*) 170.1 $[M]^+$ (cald. for $C_8H_7ClO_2$, 170.01), 135.1 $[M\text{-}Cl]^+$.

(12) Chlorination of p-methylstyrene

The reaction was carried out in fluorobenzene according to the general procedure using Ag@AgCl as catalyst to give 4-$ClCH_2$-$PhCHCH_2$ (CAS registry No: 1592-20-7) at 70% conversion and 68% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.38 (d, J=10.0 Hz, 2H), 7.34-7.32 (d, J=10.0 Hz, 2H), 6.73-6.67 (q, J=10.0 Hz, 1H), 5.77-5.74 (d, J=15.0 Hz, 1H), 5.28-5.25 (d, J=15.0 Hz, 1H), 4.56 (s, 2H); GC-MS (*m/z*) 152.1 $[M]^+$ (cald. for C_9H_9Cl, 152.03), 117.1 $[M\text{-}Cl]^+$.

(13) Chlorination of 4,4`-dimethylbiphenyl

The reaction was carried out according to the general procedure using Ag@AgCl as catalyst to give 4-$ClCH_2$-4`-CH_3-biphenyl (CAS registry No: 38580-84-6) at 83%conversion and 82% yield. GC-MS (*m/z*) 216.1 $[M]^+$ (cald. for $C_{14}H_{13}Cl$, 216.07), 181.1 $[M\text{-}Cl]^+$.

The photocatalytic halogenation of cyclohexene

The phase transfer catalyst TBAC (0.8 mmol) and Ag@AgCl photocatalyst (0.60 g) were added to the photocatalytic reaction vessel (PLS-SXE300CUV) and charged with cyclohexene (0.5 mol). Saturated sodium chloride solution (90 ml) containing concentrated hydrochloric acid (6 ml) was added to the vigorously stirred solution. A 300W xenon lamp was used as light source to irradiate the reaction mixture for 8 h and the reaction monitored by GC. The reaction mixture was filtered to reclaim the photocatalyst and the solution separated. The inorganic/aqueous phase was collected for future use and the organic phase dried ($MgSO_4$) and filtered. The chlorination product was obtained by evaporation to give a mixture of 3-chlorocyclohexene, 2-chlorocyclohexanol and 1,2-dichlorocyclohexane. GC-MS showed that the latter two were obtained in 27% and 21%, respectively, with the ratio being approximately 6:4. 3-Chlorocyclohexene was just only produced in 0.2%.

3-Chlorocyclohexene (CAS registry No:2441-97-6), GC-MS (m/z) 116.0 $[M]^+$ (cald for C_6H_9Cl , 116.04), 81.2 (M^+-Cl)

2-Chlorocyclohexanol (CAS registry No:1121-21-7), GC-MS (m/z) 134.1 $[M]^+$ (cald for $C_6H_{11}ClO$, 134.05), 116.1 (M^+-H_2O), 98.1 (M^+-HCl), 80.1 (M^+-HCl-H_2O).

1,2-Dichlorocyclohexane (CAS registry No:1561-86-0), GC-MS (m/z) 152.0 $[M]^+$ (cald for $C_6H_{10}Cl_2$, 152.02), 116.0 (M^+-Cl), 81.1 (M^+-2Cl), 80.1 (M^+-2HCl).

Conclusions

In conclusion, we have developed a highly selective halogenation method for unactivated$C(sp^3)$–H bonds. The reaction occurs readily using an aqueous NaX/HX solution as halide source under visible light or LED irradiation and air conditions and with a nanoAg@AgX catalyst at room temperature. The halogenation of saturated 5 - 8 carbons cyclic hydrocarbons results in only the corresponding mono-halide and the chlorination versus bromination conversion was higher. For cyclohexane and cyclopentane, the yields were 95% and 94%, respectively. This reaction is not only novel, but is also an efficient and highly sustainable halogenation method. Mechanism studies support the idea that the reaction is mediated by a free radical process involving blue light activation which causes AgCl bonding electrons to be excited, and hence, transfer electrons from chloride ion to induce chlorine radical formation and drive the substitution reaction.

Conflicts of interest

There are no conflicts to declare.

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